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(54) Production of porous structures having adjustable total pore volume, size and wall thickness

(57) A porous structure having an adjustable total pore volume, an adjustable pore size and an adjustable pore wall thickness is made by dissolving a polymer by heating beyond the upper critical temperature T_c in a mixture of two components A and B which are liquid and miscible at the dissolving temperature, the mixture of polymer and components A and B used having a miscibility gap in the liquid aggregate state, component A being a solvent for the polymer and component B increasing the phase separation temperature of a solution consisting of the polymer and component A, optionally forming the solution and causing it to disintegrate and solidify by cooling and optionally extracting component(s) A and/or B.

Using non-toxic substances, such as edible oils, for component A and castor oil for component B, it is possible to obtain structures, particularly membranes in the form of hollow fibres, which are non toxic and which may be safely used, for example, in the medical field and in the food industry.

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SPECIFICATION

Process for the production of porous structures having an adjustable total pore volume, an adjustable pore size and an adjustable pore wall thickness

- 5 This invention relates to a process for the production of porous structures having an adjustable total pore volume, an adjustable pore size and an adjustable pore wall thickness; more particularly, it relates to a process for the production of shaped and unshaped porous structures, such as filaments, films, flexible tubes, rods, profiles and powders, in particular to the production of membranes in the form of hollow fibres
10 having an adjustable total pore volume, an adjustable pore size and an adjustable pore wall thickness. Processes for the production of porous structures, including both macroporous and microporous structures and combinations thereof, are described in DE-OS No. 2,737,745 which mentions numerous polymers and liquids capable of being processed from a homogeneous solution by certain methods to form shaped structures having interesting properties. In this case, a particular solvent is used for a certain polymer or polymer combination.
- 15 Using this process, it is possible above all to produce shaped structures having an adjustable total pore volume. By varying the polymer content of the solution, it is possible to vary the pore volume of the finished structure within wide limits. However, difficulties are involved in adjusting pore size to a required value because the size of the individual pores increases with increasing pore volume. Although it is possible to control pore size to a certain extent by varying the cooling conditions, this may only be done within certain limits, firstly because in many cases the cooling process is very difficult to control and secondly because the forming process by which shaped structures are obtained also involves difficulties if cooling takes place under conditions differing more or less seriously from those established in advance. Thus, in the event of very slow cooling, the structures are unable to retain shape, while, in the event of over-rapid cooling, difficulties arise at the exit of the die used for forming such as hollow fibre dies.
- 25 Another disadvantage of the described process resides in the fact that a considerable number of the liquids recommended are more or less toxic so that the effort involved in extracting the toxic liquid after solidification of the shaped structure is very considerable, particularly in cases where the shaped structures are to be used, for example, in the medical field, in the pharmaceutical industry or in the food industry.
- 30 Problems similar to those discussed above may also arise in processes for the production of shaped structures of the type described, for example, in DE-OS No. 2,833,493 and in DE-OS No. 3,026,718. Accordingly, although there are numerous processes by which it is possible to obtain porous structures, there is still a need for improved processes which give products having favourable and improved properties.
- 35 Accordingly, an object of the present invention is to provide an economic process by which it is readily possible to produce shaped and unshaped porous structures having an adjustable total pore volume, an adjustable pore size and an adjustable pore wall thickness.
- Another object of the present invention is to provide a process by which these properties may be reproducibly obtained, which is highly reliable in operation and which gives structures which may be safely used, for example, in the medical field, in the pharmaceutical industry or in the food industry.
- 40 According to the present invention, these objects are achieved by a process of the type just mentioned which is characterised in that a polymer is dissolved by heating beyond the upper critical temperature T_c in a mixture of two compounds A and B which are liquid and miscible at the dissolving temperature, the mixture of polymer and compounds A and B used having a miscibility gap in the liquid aggregate state, compound A being a solvent for the polymer and compound B increasing the phase separation temperature of a solution consisting of the polymer and compound A, the solution is optionally formed and is made to disintegrate and solidify by cooling and components A and/or B are optionally extracted.
- 45 A non-solvent for the polymer may be used as component B. It is also possible to use a compound B which dissolves the polymer, but of which the dissolving temperature in relation to the polymer is at least 50°C, preferably at least 100°C, higher than the dissolving temperature of compound A in relation to the polymer. Compound B may also be a swelling agent for the polymer.
- 50 One particularly preferred embodiment of the process according to the present invention is characterised by the use of a polymer and a compound A which form a binary system having a miscibility gap in the liquid aggregate state. Suitable polymers are polyolefins, particularly polypropylene. For polyolefins, such as polypropylene, edible oils or edible fats are preferably used as component A. In that case, component B may be a compound which is miscible with edible oils or edible fats and which is a non-solvent for the polymer or of which the dissolving power for the polymer is considerably lower than that of edible oils or edible fats. In this case, castor oil is particularly suitable for use as compound B. Appropriate components A are soya oil and palm kernel oil. The solution is preferably formed into membranes in the form of hollow fibres or flat films. One particularly preferred process for the production of hollow fibre membranes involves extruding the solution into a spinning tube containing liquid A as bath liquid, the bath liquid in the spinning tube having a temperature below the phase separation temperature and the membrane and liquid A being guided through the spinning tube in the same direction at substantially the same linear speed or at only slightly different linear speeds, subsequently withdrawing the membrane from the spinning tube under slight tension and optionally extracting the hollow fibre structure formed with a solvent after it has solidified.
- 60 Another preferred process involves extruding the solution into a spinning tube containing as bath liquid a

mixture of components A and B in the same relative quantitative ratios as present in the extruded solution, the bath liquid in the spinning tube having a temperature below the phase separation temperature and the membrane and the bath liquid being guided through the spinning tube in the same direction at substantially the same linear speed or at only slightly different linear speeds, subsequently withdrawing the membrane from the spinning tube under slight tension and extracting the hollow fibre structure formed with a solvent after it has solidified.

In many cases, it has proved to be advantageous to maintain an air gap between the exit surface of the hollow fibre die used and the surface of the liquid in the spinning tube.

The liquid component A may be used in admixture with one or more other liquids, particularly other solvents. Component B may also be used in admixture with one or more other compounds. It is possible to carry out the process according to the present invention using from 5 to 90%, by weight, of polymer dissolved in from 10 to 95%, by weight, of a mixture of the liquid compounds A and B. It is preferred to use a solution containing from 15 to 30%, by weight, of polymer and from 85 to 70%, by weight, of the mixture of liquid components A and B. The mixture of A and B preferably consists of from 60 to 90%, by weight, of a solvent for the polymer and from 10 to 40%, by weight, of a non-solvent or swelling agent for the polymer.

In the context of the present invention, "porous structures" are to be understood to be shaped or unshaped structures, such as fibres, hollow fibres, tubes, flexible tubes, rods, bars or other profiles, blocks and even powders, which contain pores. The pores in question may be so-called "macropores" or "micropores" or both.

In the context of the present invention, "pores" are to be understood to be voids which may be situated both in the interior of the structure and also at its surface. It does not matter whether the voids are closed, have openings, for example at the surface of the structure or because they communicate at one or more places with the adjacent pore. The interstices through which individual voids inter-communicate and which frequently differ in dimensions from the voids which they join are also regarded as pores in the context of the present invention. The pores may assume various geometries, for example they may be in the form of elongate, cylindrical or spherical voids or even in the form of voids having a more or less irregular geometry. The radius of a pore or void is to be understood to be the radius of an equivalent hollow sphere having the same volume as the void.

Since the expression "micropores" is not consistently used in the literature so that differences between micropores and other pores cannot be explained exactly by a general definition, a micropore in the context of the present invention is to be understood to be a void having a radius of at most 30 nm.

"Macropores" are voids corresponding to the above definition of which the radius exceeds 30 nm.

The solvent for the polymer is to be understood to be a compound A in which the polymer is dissolved to form a homogeneous solution on heating to at most the boiling point of the solvent. It is obvious that, in verifying whether it is soluble in the solvent, the polymer should not be used in excessive concentrations because otherwise it is frequently no longer possible on account of the high viscosity to determine whether a homogeneous solution is in fact present. Accordingly, it is advantageous to test the dissolving power of the solvent using approximately 10% of polymer. In many cases, the solvents used have very little if any dissolving ability as regards the polymer at room temperature.

The non-solvent for the polymer is to be understood to be a component B which does not dissolve the polymer to form a homogeneous solution on heating to at most the boiling point of compound B. The components in question are preferably compounds in which the polymer is completely insoluble or only swollen under the specified conditions.

In the context of the present invention, a swelling agent which causes the polymer to swell under the above-mentioned conditions is to be understood to be a liquid which although taken up to a considerable extent by the polymer, does not lead to the formation of a single phase. By contrast, a non-solvent is taken up by the polymer to only a very limited extent, if at all, even at relatively high temperatures.

In some cases, it is also possible to use a component B which, although capable of dissolving the polymer, has a considerably reduced dissolving ability as regards the polymer compared with component A, so that, for example, to dissolve corresponding quantities of polymer it is necessary to apply a considerably higher temperature than is the case where solvent A is used.

As is apparent from the foregoing, compound A and the polymer form in the liquid aggregate state at least one region in which the system is in the form of a homogeneous solution, i.e. forms a single uniform phase in the liquid aggregate state.

When such a solution is cooled, different processes may occur. Firstly, it is possible, depending on the compound A used, for liquid/liquid separation initially to occur so that two liquid phases co-exist in the equilibrium state. On further cooling, the polymer-rich phase undergoes a drastic increase in viscosity, so that, even before actually solidifying, it may hardly be moved any more. Cooling to even lower temperatures results in the formation of one or more solid phases which may be amorphous or crystalline. Solid phase and liquid phase may co-exist over wide temperature and concentration ranges. With other types of system, no liquid/liquid separation occurs on cooling, instead a solid phase is immediately formed. These processes, which are familiar to those skilled in the art, may be illustrated by phase diagrams. Phase diagrams of the type in question may be found, for example, in the Russian works "Fibre Research, Textile Techniques" 1967 (4), 118-22 "Classification of polymer solvents" by S.P. Papkoff and S.G. Eftimova (cf in particular Figure 2, Type A II). Corresponding phase diagrams may also be found in the relevant works on physical chemistry.

The compositions of polymer and mixture A and B used must be able to be converted together into a single homogeneous liquid phase and must have an upper critical disintegration temperature below which phase separation into two liquid phases occurs. This critical disintegration temperature T_c is higher than the phase separation temperature of a solution containing equal amounts of polymer and component A - and only compound A - as liquid.

It has surprisingly been found that the pore size of the porous structures obtained may be controlled by the addition of component B in accordance with the present invention. This presupposes that compound B, when added to a system consisting of polymer and liquid component A, increases the phase separation temperature. This means, for example in the case of polymer/A systems having a miscibility gap in the liquid aggregate state, that the critical temperature T_{cl} is increased by the addition of compound B.

According to the present invention, the addition of component B to systems of polymer and compound A having no miscibility gap in the liquid aggregate state produces a system which does have a miscibility gap in the liquid aggregate state. The process according to the present invention may be used with advantage for treating mixtures in which the polymer and component A already form a system which has a miscibility gap in the liquid aggregate state. Particularly suitable polymers are polyolefins, such as polypropylene and polyethylene. Polymers based on acrylates, such as methyl acrylate and methyl methacrylate, vinyl compounds, such as vinyl chloride and vinyl acetate, and copolymers of the abovementioned monomers may also be processed in accordance with the present invention. Polyamides, polyesters, polyurethanes and polycarbonates, for example, may also be processed into porous structures in accordance with the present invention.

Solvents which are capable of performing the function of component A in relation to the polymer used are mentioned, for example, in DE-OS No. 2,737,745 to which reference has already been made. It is, of course, possible to use other suitable solvents.

For polyolefins, particularly polypropylene, the function of component A may be performed in particular by edible fats and edible oils, preferably of the vegetable-based type, such as soya oil, palm kernel oil, grapeseed oil, peanut oil, sunflower oil, corn oil, palm oil, sesame oil, safflower oil and olive oil, and vegetable fats, such as coconut fat and palm kernel fat. Fats hardened by hydrogenation may also be used.

Suitable non-solvents for polyolefins include castor oil, glycerol diacetate and triacetate, polyethylene glycol and linseed oil.

In certain cases, it is even possible to use as component B a compound which, although capable of dissolving the polymer at relatively high temperatures, has a dissolving temperature at least 50°C , preferably at least 100°C , higher than that of component A. One such preferred composition is the polyethylene/isopropyl myristate/soya oil system. In another composition, namely polyethylene/soya oil/castor oil, which is also suitable for use in accordance with the present invention, the soya oil performs the function of component A, while in the previous example it performs the function of component B. Thus, it is possible depending on the composition selected to use one and the same liquid first as compound A and then as compound B.

Suitable polymer/component A/component B compositions are given in the following Table from which it may be seen that, in certain cases, one and the same compound occurs both as compound A and also as compound B.

TABLE

<i>Polymer</i>	<i>Compound A (solvent)</i>	<i>Compound B</i>
Polypropylene	soya oil	castor oil
	palm kernel oil	castor oil
soya oil	soya oil	linseed oil
	palm kernel oil	polyethylene glycol
soya oil	grapeseed oil	polyethylene glycol
	soya oil	polyethylene glycol
	soya oil	glycerol diacetate
soya oil	soya oil	glycerol triacetate
	palm kernel oil	glycerol triacetate
	peanut oil	castor oil

	Polypropylene	sunflower oil	castor oil	
		corn oil	castor oil	
5		palm oil	castor oil	5
		sesame oil	castor oil	
		safflower oil	castor oil	
10		coconut fat	castor oil	10
		lard	castor oil	
15		goose fat	castor oil	15
		paraffin oil	castor oil	
		stearyl alcohol	polyethylene glycol 200	
20		isopropyl myristate	castor oil	20
		decanol	polyethylene glycol 200	
25		N,N-bis-(2-hydroxy-ethyl)-hexadecylamine	castor oil	25
	High-pressure polyethylene	soya oil	castor oil	
30		palm kernel oil	castor oil	30
		isopropyl myristate	castor oil	
35		isopropyl myristate	soya oil	35
	Polyamide-6 and -6,6,	ethylene glycol	glycerol	
40		ethylene glycol	polyethylene glycol	40
		glycol	polyethylene glycol 600	
		caprolactam	polyethylene glycol 600	
45		butyrolactone	polyethylene glycol 200	45
	Copolyamide based on ε-caprolactam/hexamethylene diamine adipic acid	glycerol	polyethylene glycol 600	
50				50
		caprolactam	polyethylene glycol 600	
55		butyrolactone	polyethylene glycol 200	55

5	Copolyamide based on 20 % of hexamethylene diamine adipic acid and 80% of ε-caprolactam	ethanol	water	5
		ethylene glycol	water	
10	Polymethyl methacrylate	polyethylene glycol	ethylene glycol	10
		butyrolactone	water	
15	Copolymer of vinyl chloride and vinyl acetate	ethylene glycol acetate	water	15
20		dimethylformamide	ethylene glycol	20
	Polyurethane	butyrolactone	glycerol	
25	Polycarbonate	butyrolactone	glycerol	25

The choice of other suitable combinations and, more particularly, of suitable components B does not involve serious difficulties on the basis of the general criteria involved.

The production of porous structures from the polymer/compound A/compound B solutions may be carried out by known methods using conventional dies, such as wide slot dies, profiled dies, annular-slot dies and hollow fibre dies.

It was particularly surprising to find that it is possible in accordance with the present invention to produce structures having a variety of different shapes with an adjustable pore volume, an adjustable pore size and an adjustable pore wall thickness. In this connection, the pore volume, i.e. the total pore volume which may be equated with the total number of voids in the shaped structure, may be controlled by the total content of components A and B in the mixture. A high content of A- and B-mixture also produces a high pore volume in the structure. The pore size may be controlled by the relative ratio of compound A to compound B, the pore size increasing with an increase in the relative content of B.

According to the present invention, total pore volume, pore size and pore wall thickness may be reproducibly adjusted. It is no longer necessary to use methods which operate very unreliably, such as influencing the cooling conditions or varying the concentration. Thus, it is possible for otherwise the same production conditions to adjust pore size solely by varying the relative ratio of components A and B. It is possible to produce shaped structures which may be safely used in the medical field and also in the food industry. This is because the process according to the present invention makes it possible to use compounds, particularly compounds such as edible oils, which are completely safe. In addition, the extractability of the structures in the process according to the present invention is considerably improved in many cases.

In some cases, it may be advantageous to leave either both components A and B or only one of them in the structure and to extract only one component, if any.

Thus, it is possible to avoid the occurrence of allergies which may arise in cases where shaped structures still containing traces of harmful substances are used for medical treatment.

Membranes produced in accordance with the present invention may be used in various separation processes. They may be used with particular advantage in processes in which yeast cells are filtered off, in the filtration of wine and in the manufacture of acetic acid. It is also possible to filter off numerous bacteria by means of membranes produced in accordance with the present invention.

Another particular advantage resides in the fact that additives used for improving mechanical properties, such as mineral fillers, may also be used in the process according to the present invention. Other additives may also be used.

The present invention is illustrated by the following Examples:

Example 1

A mixture of 25 parts of polypropylene (\overline{M}_w 450,000) and 75 parts of the solvent mixture of edible soya oil, standard commercial quality, and castor oil DAB 8 mentioned in Table 1, column (a) was dissolved in a heatable glass vessel. At the same time, the polymer granulate and solvent were heated to the particular dissolving temperature (Table 1, column (b)) with intensive stirring under a nitrogen atmosphere. it could

clearly be seen that, at about 155°C, the granulate became transparent and swollen with increasing temperature until, finally, a homogeneous, viscous solution was formed at the dissolving temperature. In order to guarantee satisfactory membrane formation, the solution was deaerated.

TABLE 1:

	Test No.	(a)	Solvent mixture soya oil/castor oil	(b) Dissolving temperature	Nature of the example	
10	1		100 % : 0 %	approx. 175°C	comparison	10
	2		95 % : 5 %	approx. 180°C	according to the present invention	
15	3		90 % : 10 %	approx. 185°C	"	15
	4		80 % : 20 %	approx. 195°C	"	
20	5		70 % : 30 %	approx. 210°C	"	20

The thus-prepared solution was extruded through the hollow filament die of a spinning machine into a spinning tube and processed to form hollow-filament membranes. Nitrogen was used as the internal filling. After an approximately 1 cm wide air gap, the filament passed through the approximately 2 metres long spinning tube through which cooling liquid flowed. The particular solvent mixture in which the polymer was dissolved was used as the cooling medium. The temperature was maintained at 50°C. The throughflow rate was adapted to the spinning rate.

Under the effect of the rapid cooling, the hollow filament was solidified at about 120°C and was continuously removed from the spinning tube.

The particular phase separation temperature and spinning parameters are shown in Table 2.

TABLE 2

	Test No.	Phase separation temperature	melt temperature/ die temperature	
35	1	approx. 150°C	190°C	35
40	2	approx. 155°C	190°C	40
	3	approx. 158°C	190°C	
	4	approx. 170°C	190°C	
45	5	approx. 190°C	210°C	45

After extraction of the solvent with ethanol heated to approximately 50°C, the filament was dried at 50°C. Porous membranes were obtained, differing from one another in pore volume and pore structure according to the solvent mixture used. A relatively large percentage of castor oil produced a relatively high phase separation temperature and macroporous structures.

The most important properties and characteristics are shown in Table 3.

TABLE 3:

	Test No.	Blow point bars	Maximum pore size μm	Pore volume ccl/g	Water flow 0.1 bar glcm^2/min	
5						5
	1	2.5	0.2	relatively small	0.01	
	2	2.08	0.31		0.45	
10	3	1.41	0.45		0.66	10
	4	1.28	0.50		0.85	
15	5	1.1	0.58	relatively large	1.16	15

The hollow filaments had an internal lumen of approximately 300 μm for a wall thickness of approximately 140 μm . For measuring the blow point, the hollow filaments were immersed in ethanol and filled with nitrogen from inside. The pressure at which the ethanol was displaced from the walls of the hollow filament by the nitrogen and the first gas bubbles were visible on the outside was measured. The maximum pore size may be calculated from the measured value:

$$d_{\text{max}} = \frac{0.63}{P_{\text{max}} (\text{blow point})}$$

Microscopic examination of the membrane confirmed the measured values obtained.
The pore volume was determined by mercury porosimetry.
In order to determine water flow, the hollow filament was filled from inside with distilled water under a pressure of 0.1 bar after the throughflow of water had been made possible beforehand by hydrophilisation with ethanol.

Example 2

A 25% polymer solution consisting of polypropylene (\overline{M}_w 450,000) and (A) palm kernel oil (solvent) or (B) a palm kernel oil (solvent)/castor oil (non-solvent) mixture (66 parts/34 parts) was prepared in the same way as described in Example 1.

Once again, a hollow filament spinning machine was used for membrane formation as in Example 1. The difference lay in the cooling medium used which consisted of a mixture of 66 parts of palm kernel oil and 34 parts of castor oil.

	Test no.	Solvent palm kernel oil / castor oil	Approx phase separation temp. °C	Approx dissolving temp. °C	Approx spinning temp. °C	Blow point bars	
45	(A)	100 % / 0 %	150	175	200	2.5	45
	(B)	66 % / 34 %	180	210	210	1.1	
50	Test no.	Max. pore size	Nature of the example				50
	(A)	0.25 μm	comparison				
55	(B)	0.58 μm	according to the present invention				55

Example 3

A polymer solution was prepared as in Examples 1 and 2 using a polypropylene (\overline{M}_w 450,000). In this case, soya oil was used as the solvent and glycerol triacetate as the non-solvent.

Composition of the polymer solution:

25 % of polypropylene

75 % of soya oil/glycerol triacetate in a ratio of 67.5: 32.5 parts.

A homogeneous viscous solution was obtained at a temperature of approximately 210°C. The hollow filament produced at a spinning temperature of approximately 205°C had a blow point of 1.88 bars,

corresponding to a maximum pore size of 0.34 μm .

Example 4

A 22.5% polymer solution of high-pressure polyethylene LV 1.37 in a solvent mixture consisting of 77.5 parts of isopropyl myristate and 22.5 parts of castor oil was prepared in the same way as described in Example 1. At a spinning temperature of 215°C, the extruded hollow filaments formed stable, highly porous structures after extraction with acetone and drying.

In the solvent combination selected, isopropyl myristate was the solvent and castor oil the non-solvent. The phase separation temperature was approximately 157°C.

Example 5

25 parts of polyamide-6 and 75 parts of a solvent mixture of ethylene glycol and glycerol were weighed into a flanged glass flask. In a heating bath, this mixture was rapidly heated to the necessary temperatures with intensive stirring under a nitrogen atmosphere in order to obtain a homogeneous solution (see Table below).

For membrane formation, the polymer solution obtained was coated onto a glass plate. The approximately 150 μm thick film was rapidly cooled in cold water. The initially transparent solution solidified and, with increasing pore formation, initially became milky and then completely white. After a short residence time in the cooling medium, the glycol/glycerol could be extracted, for example using warm acetone or warm water.

The membranes dried at about 50°C differed from one another in pore structure and hence in wettability with water and water absorption capacity according to the composition of the solvent mixture. Microscopic cross-sections confirm these influences.

In this batch-type process, it is advantageous to use the shortest possible dissolving times and to guarantee low water contents of the solvent used because otherwise polymer degradation is inevitable.

Test no.	Polyamide	LV	Solvent mixture ethylene glycol glycerol %	Approx dissolving temp. °C	First cloud point, approx °C	Pore type	Wettability with water
1	copolyamide based on 20 % of hexamethylene diamine adipic acid and 80 % of caprolactam	3.60	95/5	128	100	relatively large, open	very good
2	"	3.60	67/33	137	112		
3	"	3.60	33/67	148	122		
4	"	3.60	5/95	158	133	relatively small, closed	relatively poor
5	Perlon LV 2.5		95/5	147	130	relatively large, open	very good
6	"		67/33	157	138		
7	"		33/67	168	147		
8	"		5/95	177	155	relatively small, closed	relatively poor

Example 6

Using the method described in Example 5, 25 parts of polymethyl methacrylate of the type obtainable from the Rohm company under the trade name of "Plexiglasformmasse 7 N" were dissolved at approximately 150°C in 75 parts of a mixture consisting of 77% of polyethylene glycol 66 (solvent) and 23% of ethylene glycol (non-solvent), (phase separation temperature approx. 115°C).

The membrane coated onto a glass plate could be freed from the solvent using warm water. After drying highly porous structures were distinctly visible under a microscope.

Example 7

A polymer solution having a phase separation temperature of approximately 120°C was prepared from a stock mixture of polyurethane produced from polyethylene glycol 1000, diphenyl methane diisocyanate and ethylene glycol in butyrolactone, by the addition of glycerol as non-solvent.

The solution had the following composition:

25 % of polyurethane (solid)

75 % of butyrolactone/glycerol - 77:33

Membrane formation was carried out on a glass plate in the same way as in Example 5, a stable coherent film being obtained after cooling to below 60°C. Porous structures wettable with water were obtained after extraction of the solvent mixture using warm water.

For the conventional polyamides, such as polyamide-6, polyamide-12, polyamide-6,6, and numerous copolyamides, the following combinations are possible.

Component A dimethyl formamide,
dimethyl acetamide,
1,4-butane diol,
1,6-hexane diol,
sorbitol,
dimethyl propane diol

In this case, glycerol triacetate is preferred for use as component B.

(Information on the accuracy of identification of mercury porosimetry in the characterisation of porous substances, as used in the investigation of structures according to the present invention, may be found in Chemie-Ing. Techn., Vol. 38, 1966, No. 12, pages 1271-1278).

CLAIMS

1. A process for the production of a porous structure having an adjustable total pore volume, an adjustable pore size and an adjustable pore wall thickness which comprises dissolving a polymer by heating beyond the upper critical temperature T_c in a mixture of two compounds A and B which are liquid and miscible at the dissolving temperature, the mixture of polymer and components A and B used having a miscibility gap in the liquid aggregate stage, component A being a solvent for the polymer and component B increasing the phase separation temperature of a solution consisting of the polymer and component A, optionally forming the solution and causing it to disintegrate and solidify by cooling and optionally extracting component(s) A and/or B.
2. A process as claimed in claim 1, wherein a non-solvent for the polymer is used as component B.
3. A process as claimed in claim 1 or claim 2, wherein a component B is used of which the dissolving temperature in relation to the polymer is at least 50°C higher than that of component A.
4. A process as claimed in claim 3, wherein a component B is used of which the dissolving temperature in relation to the polymer is at least 100°C higher than that of component A.
5. A process as claimed in claim 1 or claim 2, wherein a swelling agent for the polymer is used as component B.
6. A process as claimed in any of claims 1 to 5, wherein a polymer and a component A which form a system having a miscibility gap in the liquid aggregate state are used.
7. A process as claimed in any of claims 1 to 6, wherein one or more polyolefins is/are used as the polymer.
8. A process as claimed in claim 7, wherein polypropylene is used as the polymer.
9. A process as claimed in claim 7 or claim 8, wherein one or more edible oils or edible fats is/are used as component A.
10. A process as claimed in claim 9, wherein component B is a compound which is miscible with edible oils or edible fats and which is a non-solvent for the polymer of which the dissolving power for the polymer is considerably lower than that of edible oils or edible fats.
11. A process as claimed in claim 10, wherein castor oil is used as component B.
12. A process as claimed in any of claims 9 to 11, wherein soya oil is used as component A.
13. A process as claimed in any of claims 9 to 11, wherein palm kernel oil is used as component A.
14. A process as claimed in any of claims 1 to 13, wherein the solution is formed into membranes in the form of hollow fibres.
15. A process as claimed in any of claims 1 to 13, wherein the solution is formed into membranes in the form of flat films.

16. A process as claimed in claim 14, wherein the solution is extruded into a spinning tube containing component A as bath liquid, the bath liquid in the spinning tube having a temperature below the phase separation temperature and the membrane and component A being guided through the spinning tube in the same direction and at substantially the same linear speed or at only slightly different linear speeds, after which the membrane is withdrawn from the spinning tube under slight tension and, after solidification, the hollow fibre structure formed is optionally extracted with a solvent. 5
17. A process as claimed in claim 14, wherein the solution is extruded into a spinning tube containing as bath liquid a mixture of components A and B in the same relative quantitative ratios as present in the extruded solution, the bath liquid in the spinning tube having a temperature below the phase separation temperature and the membrane and the bath liquid being guided through the spinning tube in the same direction at substantially the same linear speed or at only slightly different linear speeds, after which the membrane is withdrawn from the spinning tube under slight tension and, after solidification, the hollow fibre structure formed is extracted with a solvent. 10
18. A process as claimed in claim 16 or claim 17, wherein an air gap is maintained between the exit surface of the hollow fibre die used and the surface of the liquid in the spinning tube. 15
19. A process as claimed in any of claims 1 to 18, wherein the liquid component A additionally contains one or more other solvents and component B is used in admixture with one or more other compounds.
20. A process as claimed in any of claims 1 to 19, wherein from 5 to 90 %, by weight, of polymer is dissolved in from 10 to 95%, by weight, of the mixture of liquid components A and B.
21. A process as claimed in claim 20, wherein from 15 to 30%, by weight, of polymer is dissolved in from 85 to 70%, by weight, of the mixture of liquid components A and B. 20
22. A process as claimed in any of claims 1 to 21, wherein the mixture of components A and B consists of from 60 to 90%, by weight, of a solvent for the polymer and from 10 to 40%, by weight, of a non-solvent or swelling agent for the polymer.
23. A process as claimed in claim 1 substantially as herein described with particular reference to the Examples. 25